"Dielectric Properties of Low-Temperature Sintered 0.5Ba $(Zr_{0.2}Ti_{0.8})O_3$ – 0.5$(Ba_{0.7}Ca_{0.3})TiO_3$ Ceramics "

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

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in

Ceramic Engineering

By

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CERTIFICATE

This is to certify that the thesis entitled, "**Dielectric properties of Low-Temperature Sintered $0.5Ba(Zr_{0.2}Ti_{0.8})O_3 - 0.5(Ba_{0.7}Ca_{0.3})TiO_3$ Ceramics**" submitted by **Alok Patro** in partial fulfillment of the requirement for the award of **Bachelor of Technology Degree** in **Ceramic Engineering** at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

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ABSTRACT

The lead-free 0.5Ba ($Zr_{0.2}Ti_{0.8}$) O_3 – 0.5($Ba_{0.7}Ca_{0.3}$)TiO_3 have been prepared by conventional solid state reaction technique. The phase pure BZT-BCT can be prepared at 1250^{o}C. The synthesized powder can be sintered to around 98% of the theoreticaldensity at a temperature as low as 1200°C by addinga mixture of Li_2CO_3 and Bi_2O_3as a sintering aid which may form $LiBiO_2$in-situ, whereas the conventional sintering temperature is around 1400°C. Interestingly, the dielectric properties of such low-temperature sintered samples are on a par with BZT-BCT samples prepared via conventional sintering at a high temperature.It is also found that the addition of additive shifts the relative permittivity peak maxima towards room temperature.

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CHAPTER-1

GENERAL INTRODUCTION

1. INTRODUCTION

Barium titanate is a common ferroelectric materialbut its piezoelectric property is inferior compared to that of the lead-based materials such as Lead zirconate titanate (PZT).So there is aneed to develop a lead-free piezoelectric material that can compete with the high-end PZT.Modified Barium titanate is one of the prospective piezoelectric materials that may replace the toxic lead-based materials. $BaTiO_3$ is isostructural with the mineral perovskite ($CaTiO_3$) and so is referred to as 'a perovskite'.In perovskite structure, ABO_3 where 'A' and 'B' are cation elements or mixture of two or more cation elements. In the ideal perovskite crystal structure (shown in Fig 1.1), if 'A' atom is taken at the corner of the cube, then 'B' atom resides in the body centre and an oxygen atom at each face centre of the cube.

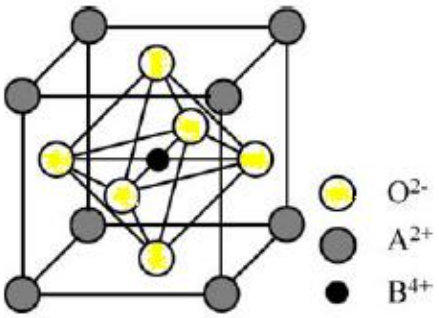
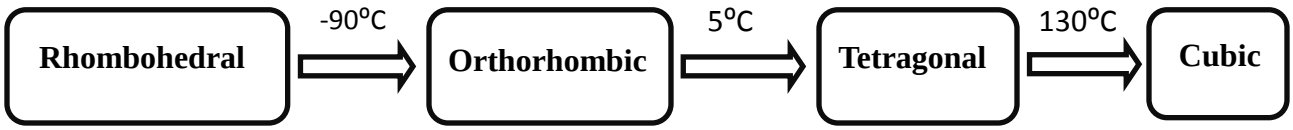


Fig.1.1Schematic Representation of Perovskite structure (ABO_3)

The perovskite structure permits wide modifications by the isovalent or aliovalentsubstituent at A or B sites with cations of approximately matching ionic radii. Barium Titanate ceramics show remarkable variation in their physical and structural characteristics with respect to 'Ca' and 'Zr' substitution.

1.1 Modification of Barium Titanate

Owing to the high relative permittivity and easy manufacturing process of Barium Titanate, it has become the first choice for applications in Multilayer Ceramic Capacitors (MLCCs).The phase transitions of $BaTiO_3$ are as follows:



These phase transitions result in higher relative permittivity near the phase transition temperatures in ε_r~T curve. For ferroelectric $BaTiO_3$, when more than one kind of ions reside in one of the available cation sub-lattices to form solid solution, then the normal sharp phase transition at T_C from ferroelectric to paraelectric state becomes diffused [1].

Doping of $BaTiO_3$ with Ca^{2+}, Zr^{4+}, etc. have been continue to be of interest for research, not only for their various applications but also for their superior dielectric and ferroelectric behaviors.Barium Zirconate Titanate ($BaZr_XTi_{1-X}O_3$, BZT) is obtained by substituting Ti ions at B-sites of $BaTiO_3$ with Zr ions. This type of substitutions reduces T_C and broadens the ε_r~T curve and also draws much attention due to the tunable structure and electrical properties to specific applications as Zr^{4+} is chemically more stable than Ti^{4+}[2].Calcium is one of the most commonly used dopants for $BaTiO_3$. It has been reported that 'Ca' ion may occupies both Ba-site and Ti-sites. When Ca^{2+} partly substitutes Ba^{2+}, it broadens the ε_r~T curve, improves electromechanical properties and restricts the formation of the unwanted hexagonal phase of $BaTiO_3$[3].

CHAPTER-2

LITERATURE REVIEW

2. LITERATURE REVIEW

Barium titanate based materials has come to the picture to replace the toxic lead based piezoelectric materials. The basic approach to attain high piezoelectricity is to bring the composition near to a composition-induced phase transition between two ferroelectric phases known as "Morphotropic Phase Boundary" in the phase diagram. Barium based compounds with perovskite structure having composition $0.5Ba(Zr_{0.2}Ti_{0.8})O_3 - 0.5(Ba_{0.7}Ca_{0.3})TiO_3$ exhibited a high piezoelectric coefficient upto 620 pC/N. It was verified that this strong piezoelectric property was due to the influence of a Morphotropic phase boundary emerging from a tetragonal-cubic-rhombohedral triple point resulting in a low energy barrier for polarization rotation and lattice distortion[4].

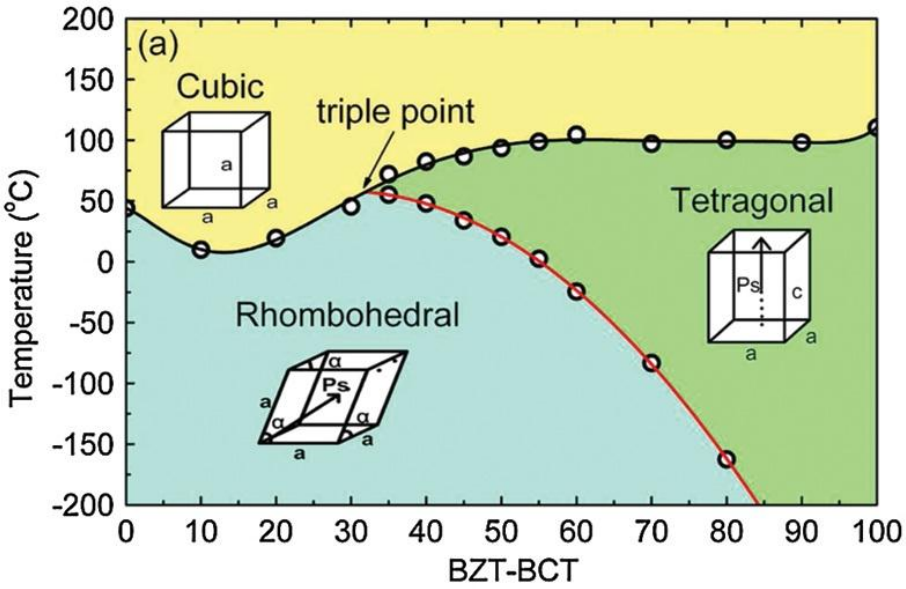


Fig 2.1 Phase diagram of pseudo-binary ferroelectric system {xBa $(Zr_{0.2}Ti_{0.8})$ O_3}-{(1-x)$(Ba_{0.7}Ca_{0.3})$ TiO_3}

The most important characteristic of this BZT-BCT system is the presence of a C-R-T triple point located at x~32% and Temprature~57^oC (shown in Fig 2.1).

Zhang et al. studied the low temperature sintering behavior of $Pb(Zr_{0.53}, Ti_{0.47})O_3$–$Sr(K_{0.25,} Nb_{0.75})O_3$ (PZT–SKN) piezoelectric ceramics with $LiBiO_2$ addition. He reported that on addition of 6 wt. % $LiBiO_2$, the sintering temperature decreases by 300-350^oC due to the generation of liquid phase. Surprisingly, the resulting samples exhibited a high-field d33piezoelectric coefficient of 415 pm/V with a Curie temperatureT_c of around 3511C, dielectric constant of 1235, and planarcoupling factor k_p of 0.54 [5].

Mazumder et al. synthesized phase-pure nanoparticles of PZT using citrate-nitrate auto-combustion method by monitoring the citrate to nitrate ratio. They found out that the 95% of the theoretical density could be achieved by adding 3 wt.% $LiBiO_2$ and sintering the synthesized powder at 715oC and the density can be improved till 97% with 2 wt.% addition and 750^oC sintering temperature. They came to a successful finding where the dielectric and piezoelectric properties of LBO added sintered samples were on par and better in some cases compared to the high –temperature conventionally sintered PZT without LBO addition [6].

Ouedraogo et al. studied the effect of CuO on $BaTiO_3$ and concluded that the cubic-quadratic transition of $BaTiO_3$ is influenced by Cu; T_M decreases and the transition becomes more diffuse with the dopant concentration. For very large quantities of inserted ions, this transition could disappear. Also for percentages higher than 0.3%, it is found from the ion concentration determination that the most probable site for Cu^{2+} is the Ti^{4+} state [7].

Vittayakorn et.al. investigated the dielectric properties of bismuth doped barium titanate ceramics by conventional solid-state method.XRD of the fabricated samples revealed only a

monophasic perovskite for the reference BaTiO3 and the properties like density, dielectric constant linearly increased with the sintering temperature. The maximum transition temperature was observed at 135oC with a relative permittivity at 1 KHz. Above the Curie temperature, the relative permittivity followed Curie-Weiss law [8].

Wu et al. studied the effect of Bi_2O_3 on the microstructure and dielectric properties of $BaTiO_3$ based ceramic systems sintered at low temperatures. He reported that addition of small amounts of $BaTiO_3$ reduced the sintering temperature from 1300^oC to 1130^oC and the bulk density increased with increasing Bi_2O_3. The dielectric constant increased upto 0.8 mol% Bi_2O_3 additive while the dielectric loss decreased [9].

Caballero et al. stated that when ZnO is used as the dopant precursor in $BaTiO_3$, ZnO redistribution takes place while heating by vapour-phase transport and grain boundary diffusion as no liquid phase formation takes place till 1400^oC. Also the sintering is assumed to take place by solid-state diffusion due to the same reason of no detection of liquid till 1350^oC. They have observed that the ZnO gets strongly segregated at the grain boundaries because of its very low solubility (less than several thousand ppm). They found out that density of materials doped with solid ZnO went as high as 99% for sintering temperatures 100^oC lower than for undoped BaTiO3. Considering the electrical parameters, dielectric constants between 2000-3000 were measured for the ZnO-doped samples. Even the dielectric losses were well below 1% for all the ZnO-doped samples, even for samples with huge concentrations of dopants. All these properties induced ZnO-doped $BaTiO_3$ to be used for high-quality capacitors and the heavily doped samples can be applied in the field of capacitor-varistor integration [10].

2.1 SUMMARY OF THE LITERATURE REVIEW:

From the literature review it can be summarized that BZT-0.5BCT shows very high dielectric constant at room temperature also with excellent piezoelectric property. The sintering temperature for this material is more than 1400^{o}C. It is well known that for fabrication of Multilayer Ceramic Capacitor and Multilayer Actuator co-firing of metal electrodes and ceramics is required. So the lowering of the sintering temperature is urgently needed. So it will be interesting to study the effect of different sintering aid on sintering and final electrical properties of this material. There are no such literatures available on low temperature sintering of BZT-BCT ceramics. It has been found that $LiBiO_2$ or mixture of Li_2CO_3 and Bi_2O_3 is very effective in Lead based piezoelectric (e.g. PZT, PMN-PT) for lowering of sintering temperature without degrading the dielectric and piezoelectric properties.

2.2 OBJECTIVE

The objective of the present work is to decrease the sintering temperature of BZT-BCT using a mixture of Li_2CO_3 and Bi_2O_3 as a sintering aid. The specific objectives of the present studies are as follows:

- Synthesis of phase-pure Ba $(Ti_{0.8}Zr_{0.2})$ O_3 – $(Ba_{0.7}Ca_{0.3})$ TiO_3i.e. $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$ by conventional solid-state reaction route.
- Studies on the sintering behavior of BZT-BCT ceramics with above mentioned additives
- Study the phase composition and purity of the prepared BZT-BCT samples.
- To study the dielectric property of sintered samples.
- To study the temperature dependence of the dielectric properties of the modified samples.
- Study the microstructure of the sintered ceramics.

CHAPTER-3

EXPERIMENTAL WORK

EXPERIMENTAL PROCEDURE

The lead free 0.5Ba ($Zr_{0.2}Ti_{0.8}$) O_3 – 0.5($Ba_{0.7}Ca_{0.3}$)TiO_3 [can be represented as ($Ba_{0.85}Ca_{0.15}$) ($Ti_{0.9}Zr_{0.1}$)O_3] was prepared by conventional solid-state reaction route. Raw materials are $BaCO_3$, ZrO_2, TiO_2, and $CaCO_3$. Calculated amounts of raw materials were weighed and kept into a planetary mill pot with ZrO_2 balls as the grinding media. Wet milling using isopropanol was done for 10 h after which the mixture was dried under IR lamp. The powder was then calcined at 1250^oC for 2 hours.

Calculated amount of Li_2CO_3 and Bi_2O_3 was added to the BZT-BCT powder so that during sintering it can produce $LiBiO_2$(LBO) in situ. The additive oxides were added in such a way so that finally 3, 5, 7 wt% $LiBiO_2$ (designated as 3LBO, 5LBO, 7LBO respectively) formed in-situ. This mixture was pot milled for 12 h and then dried. After drying, the powder was takenout and wet mixed in agate mortar using isopropanol for 30 minutes and then dried under IR lamp. This process was repeated 3-4 times for each concentration of additive. Finally this was mixed thoroughly with few drops of 3 wt. % PVA solution and uniaxially pressed into pellets at 4.2 ton and 90 sec dwelling time. Then pellets were sintered at 1200^oC for different soaking period (4,6 and 8 hr.)and taken for further characterization. Fig 3.1 describes the steps for powder preparation and sintering.

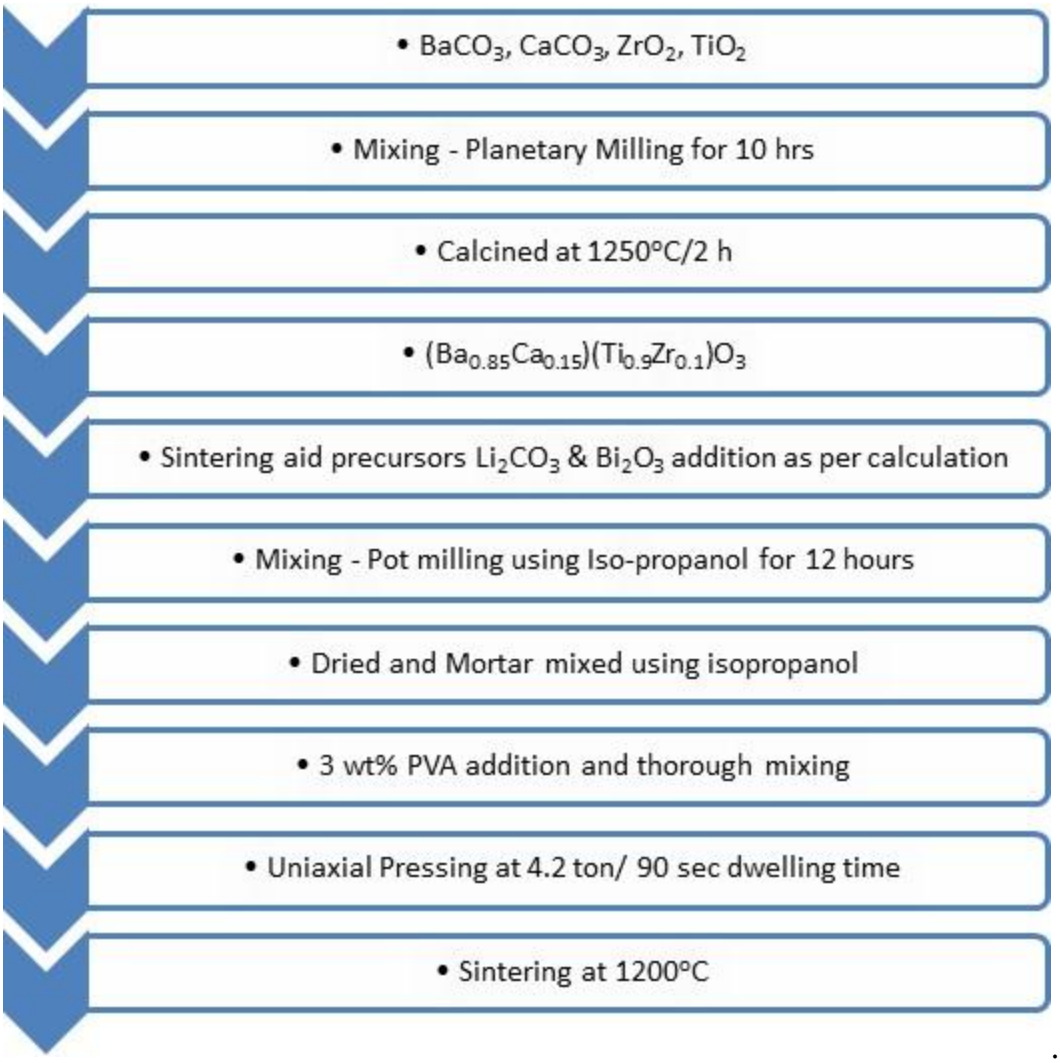


Fig 3.1 Flow chart for the powder synthesis and sintering

The phase evolution of the calcined powder and sintered ground pellets werecharacterized by X-Ray Diffraction Technique (Philips PANalytical, The Netherlands) using Cu K_α (0.154nm) radiation. Throughout the process, the generator voltage and current was fixed at 3 KV and 25 mA. Scanning of the samples was done between 2θ ranges 15 to 70^o range in continuous scan mode with 0.025^o/sec scan rate. Phases present in the sample was identified by the search-match facility available with Philips X'Pert High Score Software.

Samples were polished and ultrasonicated with acetone to remove the powder debris from the surface. Microstructural and Compositional analysis was done using Scanning Electron Microscope (JEOL-JSM 6480LV) at applied generator voltage of 15 KV.

Density Measurement by Archimedes principle

The Bulk Density and Apparent Porosity of the sintered pellets were determined by Archimedes principle using the following formulas:

$$\text{Bulk Density} = \frac{W_d}{W_S - W_a} \times \text{densityofliquidmedium}$$

$$\text{Apparent Porosity}(\%) = \frac{W_S - W_d}{W_S - W_a} \times 100$$

where W_d is the Dry Weight of the sample

W_s is the Soaked Weight of the sample

Wa is the Suspended Weight of the sample

Kerosene was used as the liquid medium (sp.gr.0.81715).

For dielectric measurement, samples were polished and then ultrasonicated using acetone to wash away the fine debris on the pellet surface. The clean samples were next electroded with silver paste followed by curing at 500^{o}C for 30min.Dielectric measurement was carried out using Solatron 1296 impedance analyzerin frequency range of 1 Hz to 1MHz.Dielectric property has also studied as a function of temperature.

CHAPTER-4

RESULTS AND DISCUSSION

4. Result and Discussion

4.1 X-ray analysis

Fig.4.1 shows the X-ray diffraction patterns of the BZT-BCT ceramics calcined at 1250^{o}C. It can be observed that pure perovskite phase produced, also suggesting that the Ca and Zrhave diffused into the $BaTiO_3$ lattice side to form a solid solution. No secondary peak was found in thisBZT-50BCT ceramic.The BZT-BCT ceramic possesseddominant tetragonal crystal structure and it was matched with JCPDS card no 75-2119.

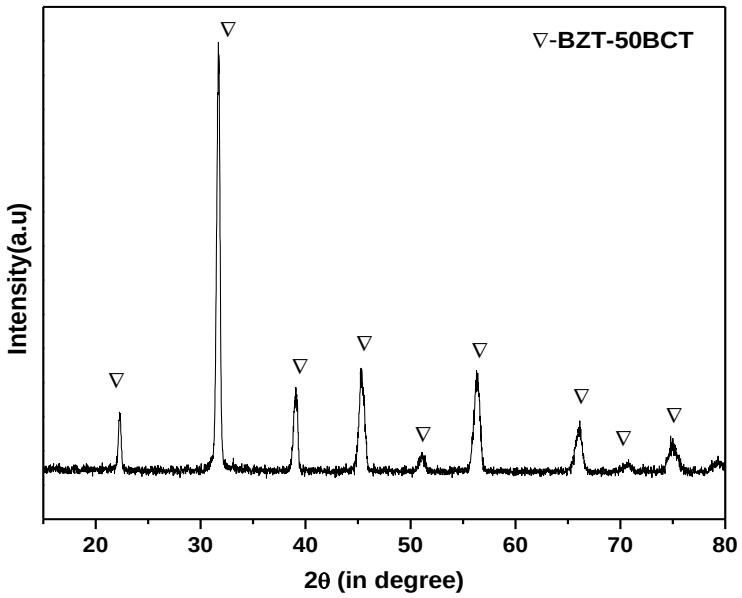


Fig .4.1 X-ray pattern of BZT-50BCT ceramic calcined at 1250^{o}C

Fig.4.2. shows the X-ray diffraction patterns of the different LBO added BZT-BCT ceramic sintered 1200^{o}C.

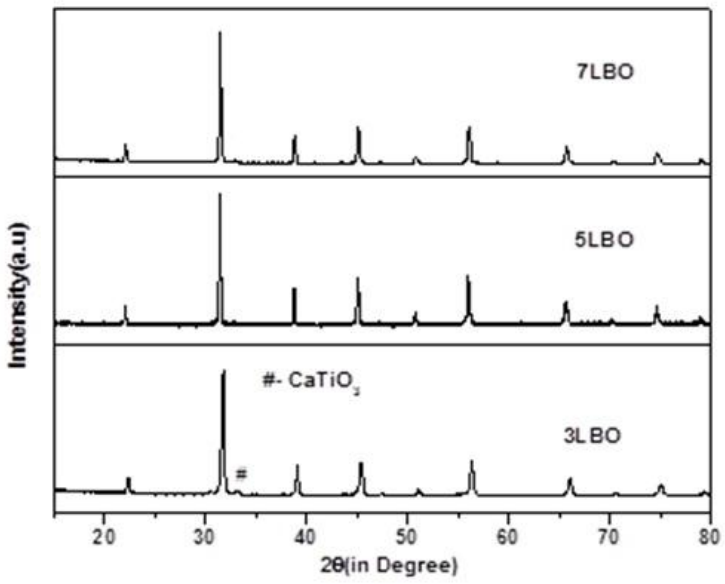


Fig. 4.2 X -ray diffraction patterns of LBO added BZT-BCT ceramic sintered at 1200^{o}C

It can be observed that 3LBO sample show avery small impurity phase of $CaTiO_3$ with JCPDS card no.820230 while5LBO and 7LBO exhibited a pure perovskite phase and no secondary phase containing Li and Bi was observed.

4.2 DILATOMETRY:

Fig 4.3 shows the dilatometric curve of pure BZT-BCT and 5LBO added BZT-BCT green compact. It can be observed thatonset temperature of shrinkage starts at around 700^{o}C for 5LBO sample while for pure BZT-BCT ceramic starts at 1200^{o}C. At around 1200^{o}C, a reasonable shrinkage occurred for 5LBO sample. The melting temperature of Li_2CO_3, Bi_2O_3, and $LiBiO_2$ are 723^{o}C, 820^{o}C and 700^{o}C respectively. In-situ formation of $LiBiO_2$may be the reason for starting of shrinkage around 700^{o}C.

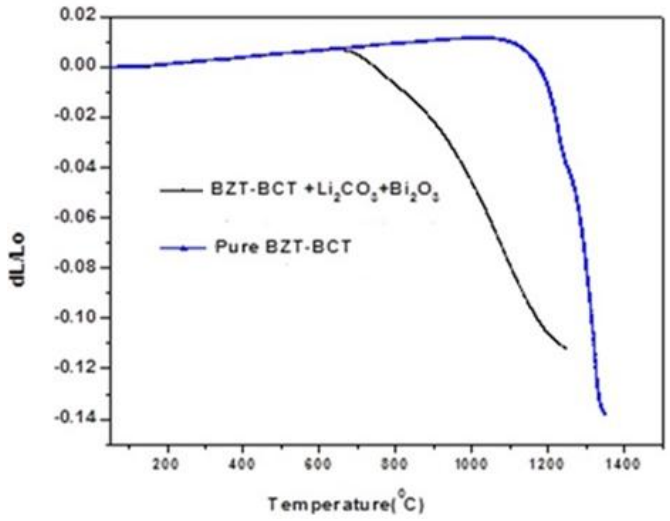


Fig .4.3Dilatometrycurve of Pure BZT-50BCT and 5LBO ceramic.

4.3 BULK DENSITY:

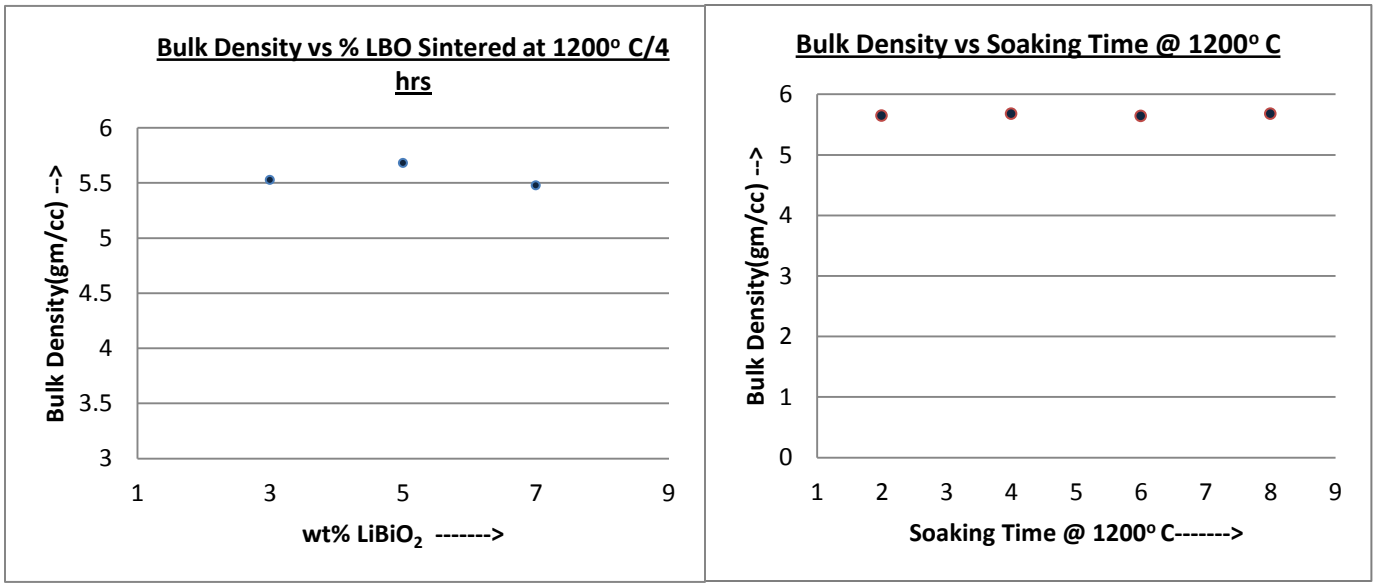


Fig .4.4Plot for (a)Bulk Density vs % LBO Sintered at 1200° C/4 hrs.

(b) Bulk Density vs Soaking Time @ 1200° C

	Sintering Temperature	Soaking Time (H)	Bulk Density (gm/cc)
3wt%LBO	**1200^{o}C**	**4**	**5.525**
5wt %LBO	**1200^{o}C**	**2**	**5.644**
		4	**5.679**
		6	**5.64**
		8	**5.676**
7wt%LBO	**1200^{o}C**	**4**	**5.477**

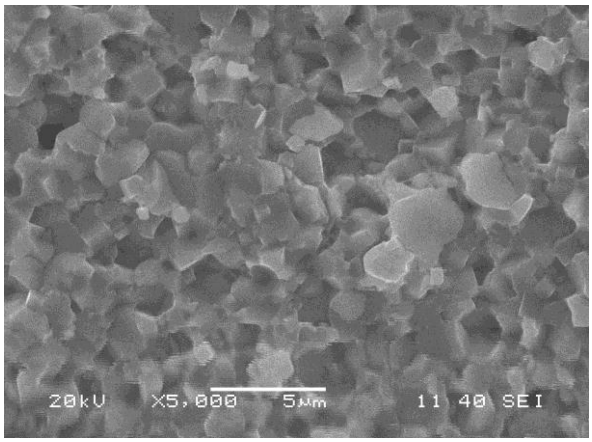
Table 1 Bulk Density of different LBO samples

Fig 4.4(a) shows the bulk density of different LBO added ceramics sintered at 1200^{o}C. The density of the sample increases with increasing LBO content upto 5wt% then it decreases. It can be observed the maximum density is attained in case of 5LBO sample. It may be that higheramount of LBO addition produces excessive liquid phase which degrades sintering. Fig 4.4 (b) shows that there is no significant change in density of 5LBO ceramics with increasing soaking time. Further studies are required for proper understanding of the phenomena. The density of different LBO ceramics is shown in table 1.

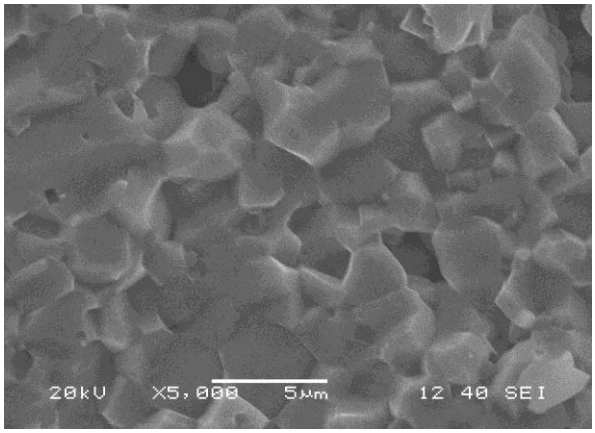
4.4 MICROSTRUCTURAL ANALYSIS

Fig.4.5. shows the SEM micrographs of the fracture surface of different LBOadded sintered ceramicswhich aresintered at 1200^{o}C for 4h. The introduction of LBO plays an important role in microstructural development of modified BZT-BCT ceramics. The micrographs show that all the

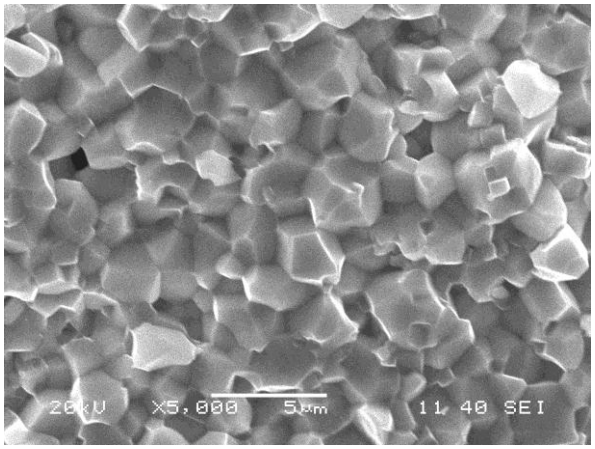
LBO sintered samples are highly dense.It is observed that LBO addition increases the grain size of sintered ceramics.



(a) BZT–BCT + 3 wt. % LBO



(b) BZT–BCT + 5 wt. % LBO



(c) BZT-BCT + 7 wt. % LBO

Fig.4.5. SEM photomicrographs of the fracture surface (a) BZT–BCT + 3 wt. % LBO (b) BZT – BCT + 5 wt. % LBO (c) BZT – BCT + 7 wt. % LBO sintered at 1200^{o}C/4 hrs.

4.5 DIELECTRIC MEASUREMENT

4.5.1 Dielectric Measurement with frequency

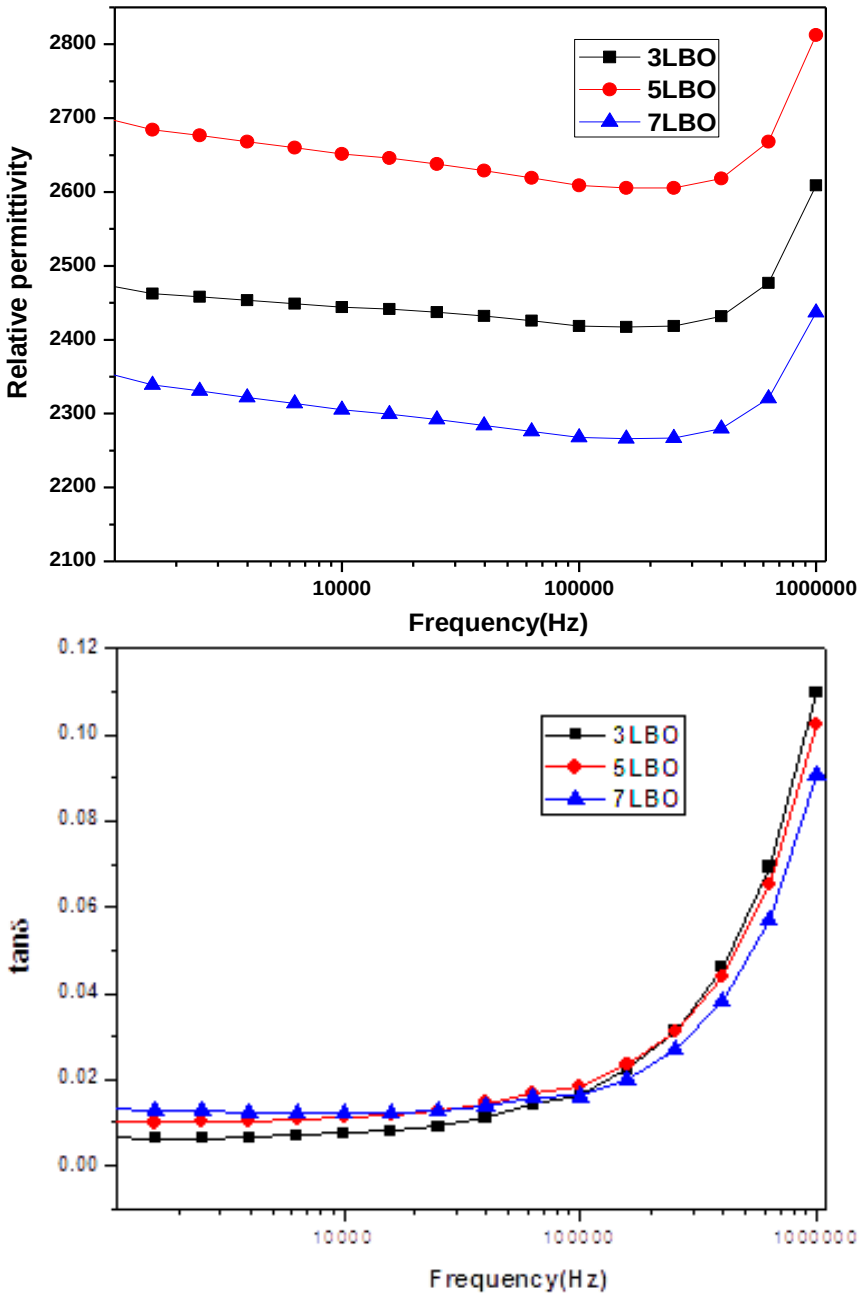


Fig.4.6 Variation of (a) Relative permittivity (ε) and (b) loss factor(tan δ) with frequency forLBOadded BZT-BCT ceramics sintered at 1200°C/4 hrs.

The frequency dependence of relative permittivity and loss tangentof different LBO added samples is shown in Fig 4.6 (a) & (b) at room temperature. It can be seen that the permittivity values of 5LBO samples are higher than that of 3LBO and 7LBO. Higher permittivity in 5LBO samplemay be due to the higher density compared to other LBO added samples. The decrease in relative permittivity for more than 5 wt%LBO addition can be explained by considering the non-ferroelectric low-ε LBO rich grain boundaries, as Wang et al. showed by XPS analysis that some LBO remains at the grain boundaries of the sintered ceramics [11].Also with LBO addition, the loss factor (at low frequencies) decreases due to the formation of non-ferroelectric LBO rich grain boundaries.

4.5.2 Dielectric measurement with Temperature

Fig.4.7 shows the temperature dependence of relative permittivity (ε) and loss tangent (tanδ) of different LBO added samplesat 1 kHz. It can be observed that with addition of LBO content, the maxima in permittivity shifts towards the room temperature. For pure BZT-BCT peak in permittivity found at around 91^{o}C. The shifting may be due to small amount of lithium and bismuth doping in perovskite structure as Li^{+} can replace Ba^{2+} in BZT-BCT (acceptor doping).Also owing to its small ionic radius, Li^{+} can stay in the intersticesand some Bi^{3+} can also replace Ba^{2+} (donor doping) [12].

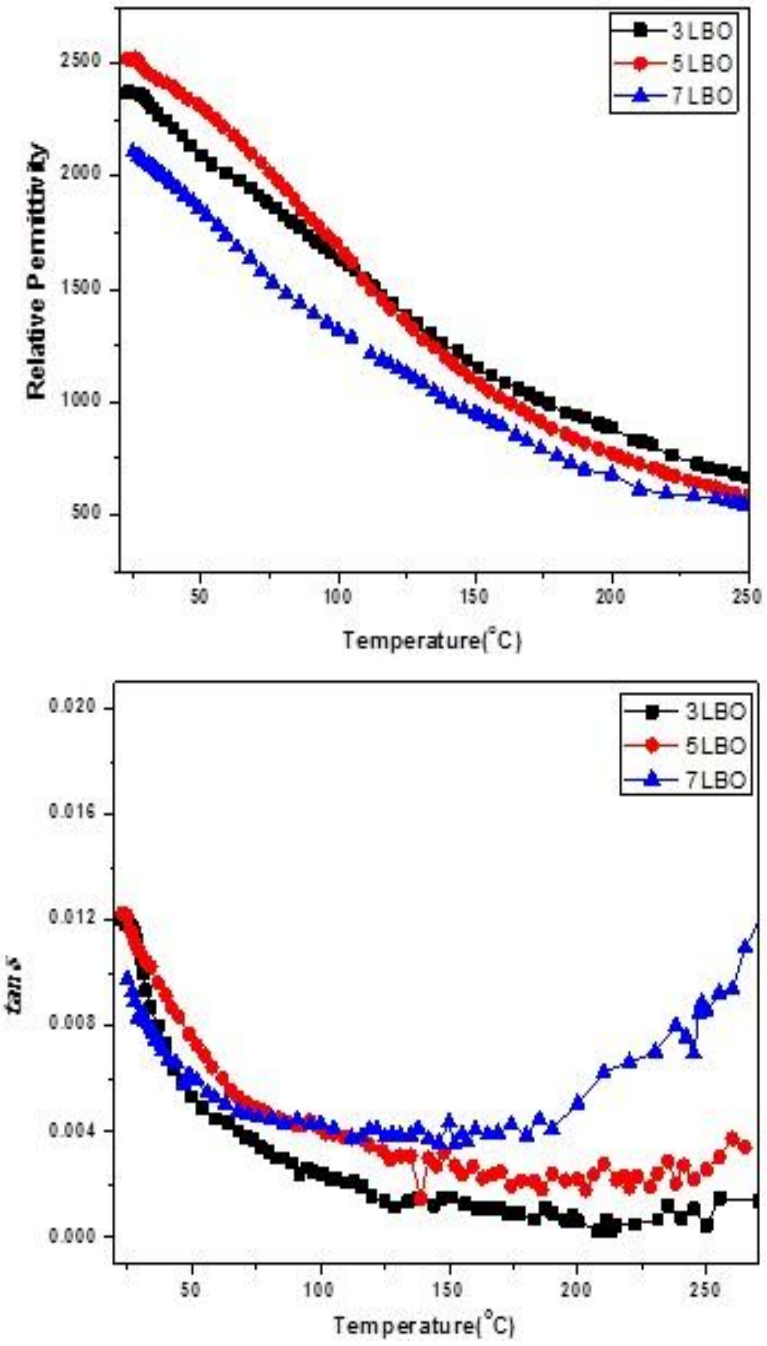


Fig.4.7Temperature dependence of (a) relative permittivity (ε) and (b) loss factor (tanδ)of different LBO sample sintered at 1200°C for 4 hrs.

CHAPTER-5

CONCLUSION& REFERENCES

CONCLUSIONS

Lead free BZT-0.5BCT was successfully sintered at 1200^{o}C with addition of a mixture of Li_2CO_3 and Bi_2O_3as a sintering aid which form $LiBiO_2$in-situ. 98% of theoretical density was achieved for 5 wt.% of LBO addition. It is interesting to note that relative permittivity values are not deteriorated much with this addition. The LBO addition shifts the relative permittivity peak maxima towards room temperature which is due to the Li^{+} and Bi^{3+} ion incorporation into the perovskite structure.

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